Electronic Supplementary Material (ESI) for RSC Advances.

Random Anion Distribution in MS_xSe_{2-x} (M=Mo, W) Crystals and Nanosheets

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SUPPORTING INFORMATION

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1. Rietveld refinement of synchrotron X-ray powder diffraction data

Rietveld refinements were carried out as described in the text. The z-parameters for S and Se were allowed to float throughout the refinement. However, they were kept equal to each other to maintain $P6_3/mmc$ symmetry. Preferred orientation along the c-axis was used as a parameter in the refinement. A preferred orientation of 1 is for an ideal case where there is no preferred orientation. Examples of refined XRD patterns are shown in Figures S1 and S2.

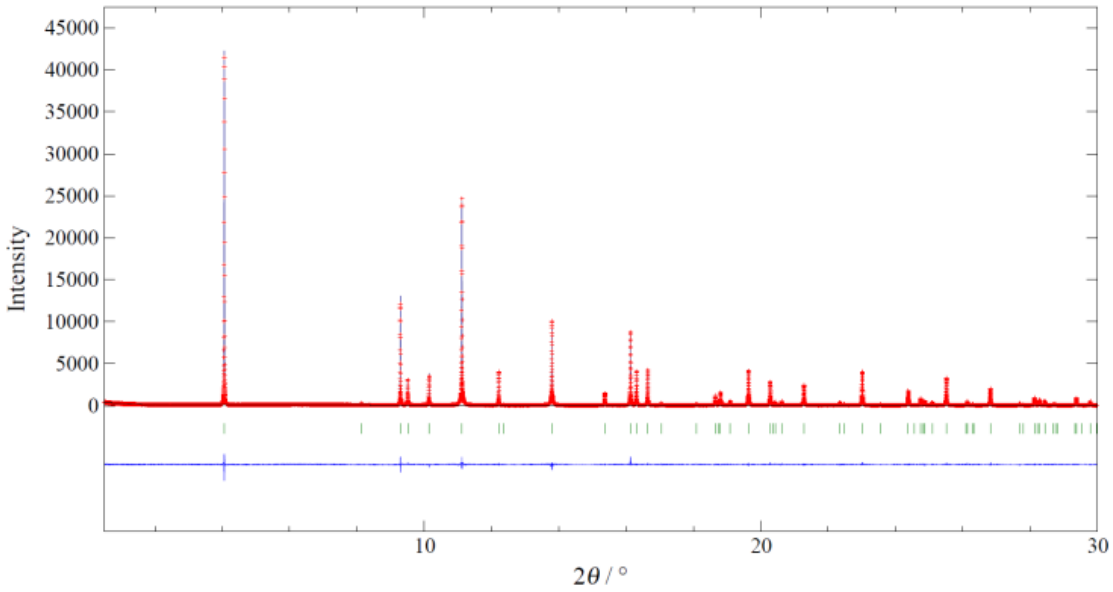


Figure S1.1. Rietveld refinement of $WS_{0.2}Se_{1.8}$.

Table S1.1. Rietveld refinement results for WS_xSe_{2-x} solid solutions.

Sample	Atom	Site	x	y	z	Preferred orientation
WS_2	W1	2d	2/3	1/3	0.25	0.999853
a/b = 3.15939 ± 0.00003	S1	4f	1/3	2/3	0.122843	
c = 12.3519 ± 0.00015						
R_p = 7.9						
$WS_{1.8}Se_{0.2}$	W1	2d	2/3	1/3	0.25	0.900451
a/b = 3.17018 ± 0.00004	S1/S	4f	1/3	2/3	0.122554	
c = 12.46440 ± 0.00027	S2/Se	4f	1/3	1/3	0.122554	
R_p = 7.1						
$WS_{1.6}Se_{0.4}$	W1	2d	2/3	1/3	0.25	1.00417

a/b = 3.18468 ± 0.00007 c = 12.47804 ± 0.0004 R_p = 8.1	S1/S S2/Se	4f 4f	1/3 1/3	2/3 2/3	0.120308 0.120308	
$WS_{1.4}Se_{0.6}$ a/b = 3.19733 ± 0.00004 c = 12.54111 ± 0.0002 R_p = 8.6	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.118441 0.118441	1.05556
$WS_{1.2}Se_{0.8}$ a/b = 3.20997 ± 0.00005 c = 12.60418 ± 0.00026 R_p = 9.9	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.119787 0.119787	1.08693
WSSe a/b = 3.22261 ± 0.00002 c = 12.66725 ± 0.0001 R_p = 11.9	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.11674 0.11674	1.7259
$WS_{0.8}Se_{1.2}$ a/b = 3.23526 ± 0.00004 c = 12.73032 ± 0.00015 R_p = 10.0	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.119199 0.119199	
$WS_{0.6}Se_{1.4}$ a/b = 3.24790 ± 0.00004 c = 12.79339 ± 0.00015 R_p = 9.4	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.120658 0.120658	1.04354
$WS_{0.4}Se_{1.6}$ a/b = 3.26055 ± 0.00004 c = 12.85646 ± 0.00024 R_p = 8.0	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.120825 0.120825	1.33194
$WS_{0.2}Se_{1.8}$ a/b = 3.27319 ± 0.00002 c = 12.91953 ± 0.00005 R_p = 8.4	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.120299 0.120299	0.980661
WSe_2 a/b = 3.28584 ± 0.00001 c = 12.98260 ± 0.00008 R_p = 8.0	W1 S1/S S2/Se	2d 4f 4f	2/3 1/3 1/3	1/3 2/3 2/3	0.25 0.121394 0.121394	0.995351

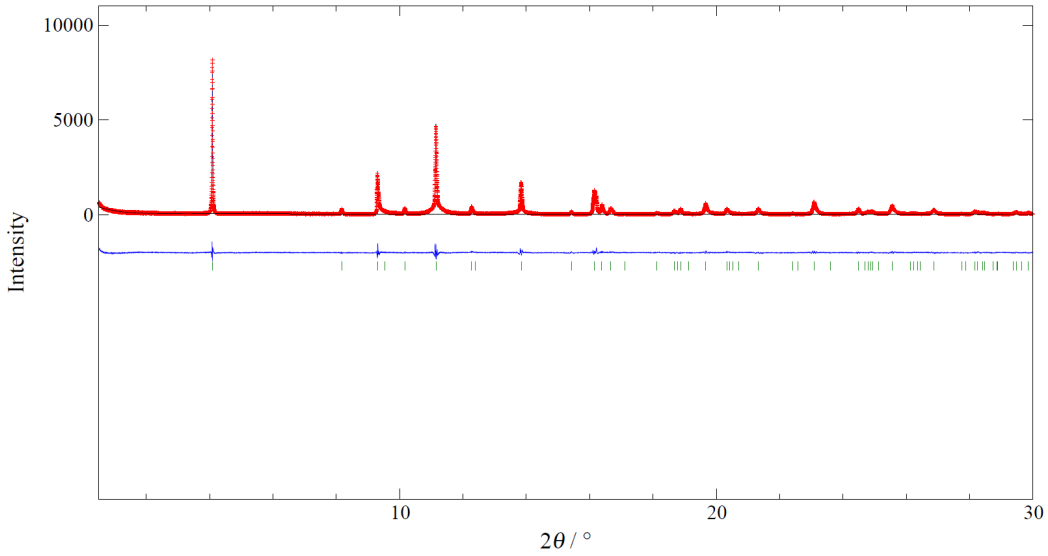


Figure S1.2. Rietveld refinement of $MoS_{0.2}Se_{1.8}$.

Table S1.2. Rietveld refinement results for MoS_xSe_{2-x} solid solutions.

Sample	Atom	Site	x	y	z	Preferred orientation
MoS_2	Mo1	2c	1/3	2/3	0.25	1.01537
a/b = 3.16224 ± 0.00011	S1	4f	1/3	2/3	0.624611	
c = 12.29399 ± 0.00090						
R_p = 5.37						
$MoS_{1.8}Se_{0.2}$	Mo1	2c	1/3	2/3	0.25	0.909656
a/b = 3.17291 ± 0.00007	S1/S	4f	1/3	2/3	0.622098	
c = 12.37002 ± 0.00045	S2/Se	4f	1/3	2/3	0.622098	
R_p = 12.4						
$MoS_{1.6}Se_{0.4}$	Mo1	2c	1/3	2/3	0.25	0.863259
a/b = 3.18372 ± 0.00004	Mo1/S	4f	1/3	2/3	0.620147	
c = 12.47169 ± 0.00020	S2/Se	4f	1/3	2/3	0.620147	
R_p = 12.2						
$MoS_{1.4}Se_{0.6}$	Mo1	2c	1/3	2/3	0.25	0.913242
a/b = 3.19442 ± 0.00003	S1/S	4f	1/3	2/3	0.619961	
c = 12.54590 ± 0.00017	S2/Se	4f	1/3	2/3	0.619961	
R_p = 10.6						
$MoS_{1.2}Se_{0.8}$	Mo1	2c	1/3	2/3	0.25	0.913567

a/b = 3.20475 ± 0.00004 c = 12.61090 ± 0.00021 R_p = 9.32	S1/S S2/Se	4f 4f	1/3 1/3	2/3 2/3	0.620549 0.620549	
MoSSe a/b = 3.22052 ± 0.00006 c = 12.69650 ± 0.00023 R_p = 11.6	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.61985 0.61985	1.56051
$MoS_{0.8}Se_{1.2}$ a/b = 3.23190 ± 0.00006 c = 12.74900 ± 0.00026 R_p = 9.82	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.619794 0.619794	1.31168
$MoS_{0.6}Se_{1.4}$ a/b = 3.24862 ± 0.00003 c = 12.80990 ± 0.00012 R_p = 8.35	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.619845 0.619845	1.41529
$MoS_{0.4}Se_{1.6}$ a/b = 3.26225 ± 0.00007 c = 12.85850 ± 0.00045 R_p = 13.6	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.62126 0.62126	1.42509
$MoS_{0.2}Se_{1.8}$ a/b = 3.26941 ± 0.00003 c = 12.89550 ± 0.00017 R_p = 10.2	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.620912 0.620912	0.844457
$MoSe_2$ a/b = 3.28591 ± 0.00006 c = 12.93751 ± 0.00023 R_p = 11.6	Mo1 S1/S S2/Se	2c 4f 4f	1/3 1/3 1/3	2/3 2/3 2/3	0.25 0.621241 0.621241	0.980848

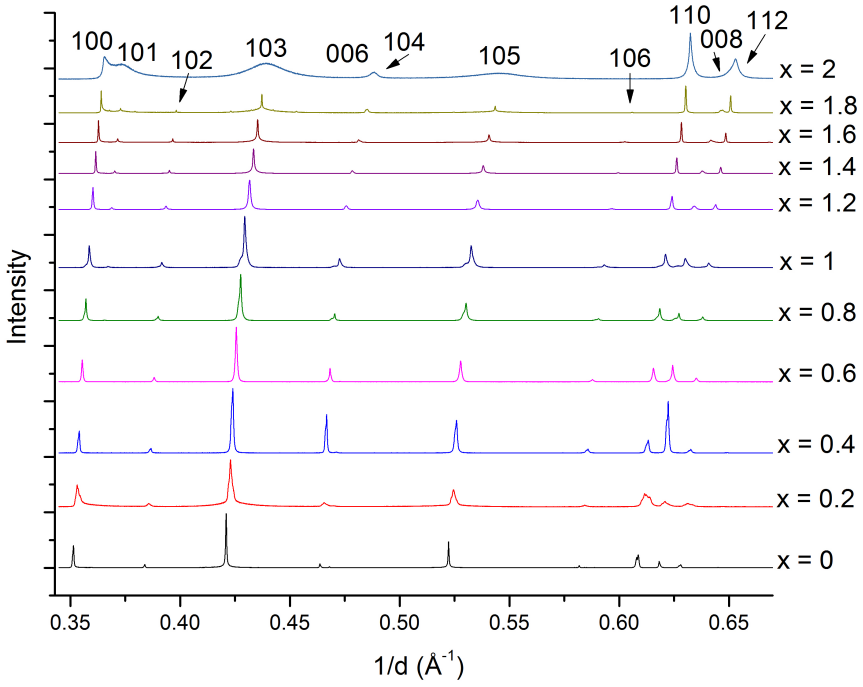


Figure S1.3. Synchrotron XRD patterns of MoS_xSe_{2-x} solid solutions. The intensities are normalized to the 100 reflection of $MoSe_2$.

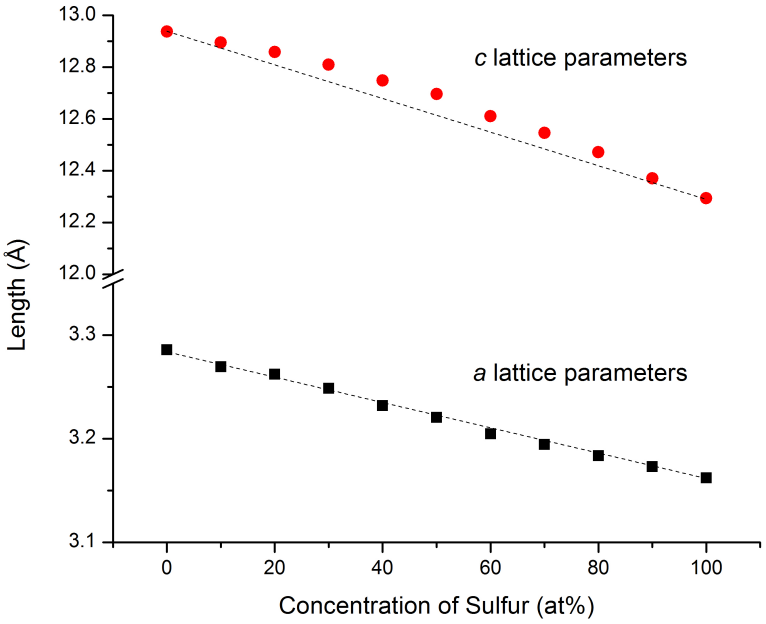


Figure S1.4. *a* and *c* lattice parameters of MoS_xSe_{2-x} solid solutions as determined from Rietveld refinement of SXRD patterns. The black lines represent the theoretical values calculated from the end members by using Vegard's law. The error bars are smaller than the size of the plot symbols.

2. Characterization of crystal morphology and composition

All energy-dispersive X-ray spectroscopy spot and mapping experiments on the WSSe solid solutions samples were conducted using a calibrated FEI Quanta 200 Environmental Scanning Electron Microscope. The maps showed homogeneous distribution of W, S, and Se within the resolution of the technique for the bulk materials.

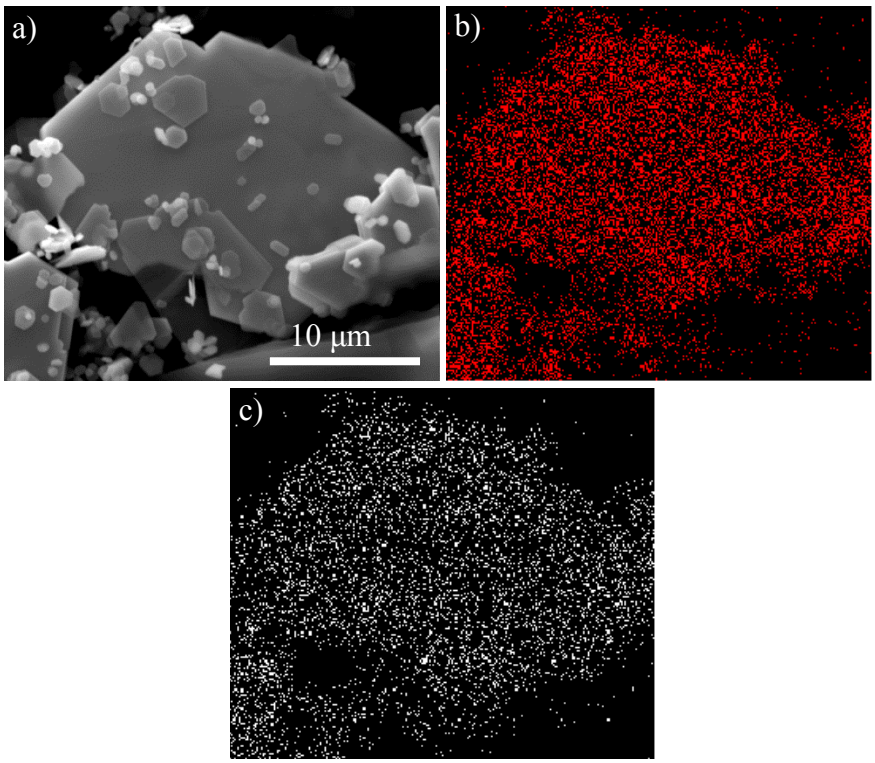


Figure S2. 1 SEM micrograph of WS_2 (a) and EDX mapping of sulfur (b) and tungsten

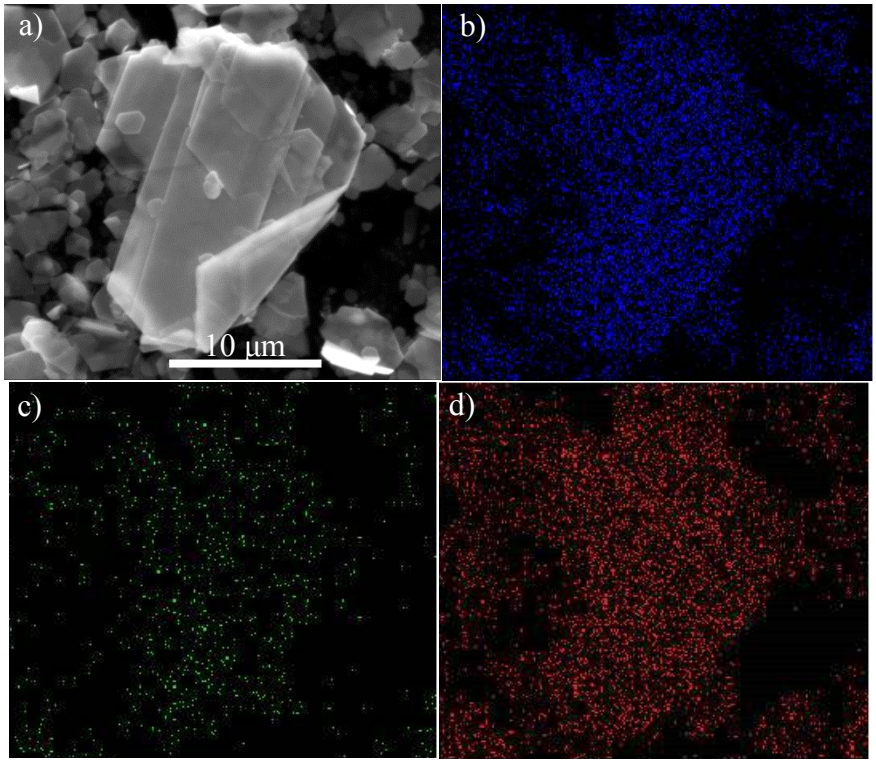


Figure S2.2 SEM micrograph of $WS_{1.8}Se_{0.2}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

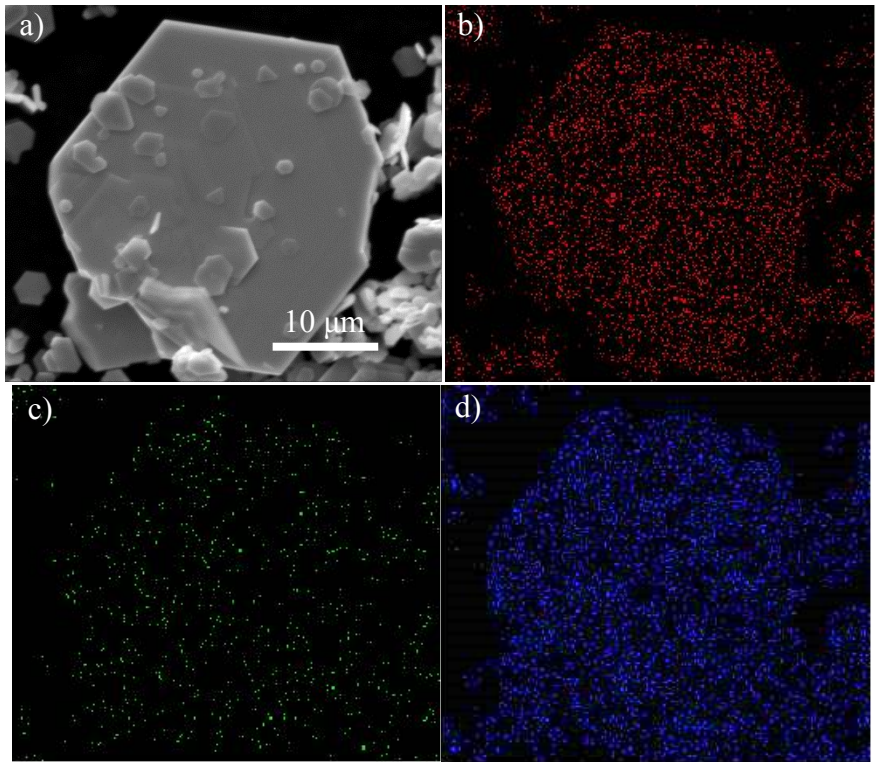


Figure S2.3 SEM micrograph of $WS_{1.6}Se_{0.4}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

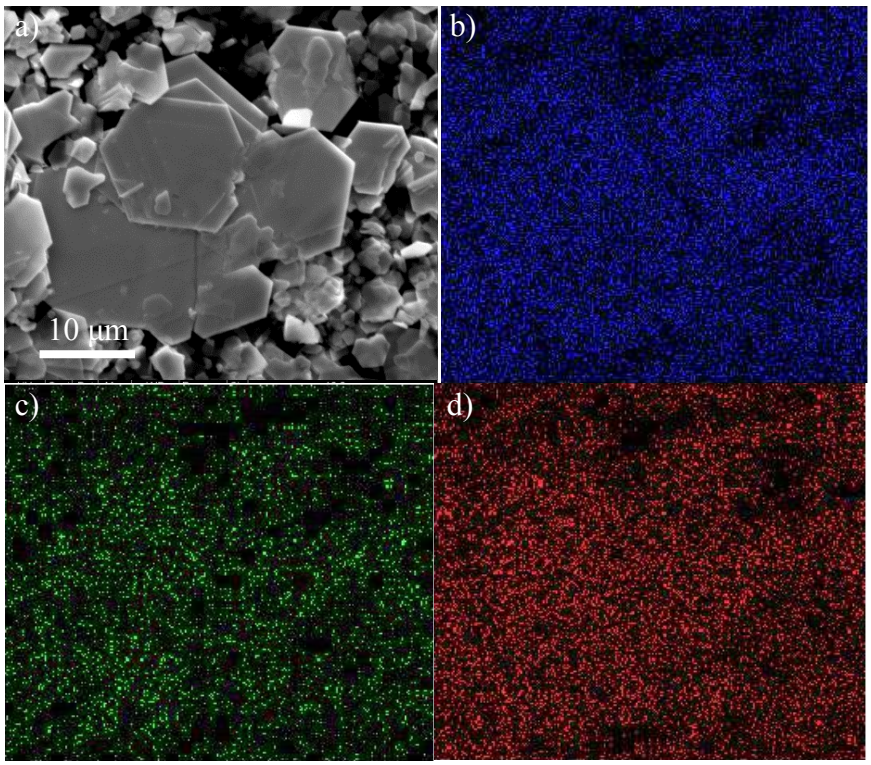


Figure S2.4 SEM micrograph of $WS_{1.2}Se_{0.8}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

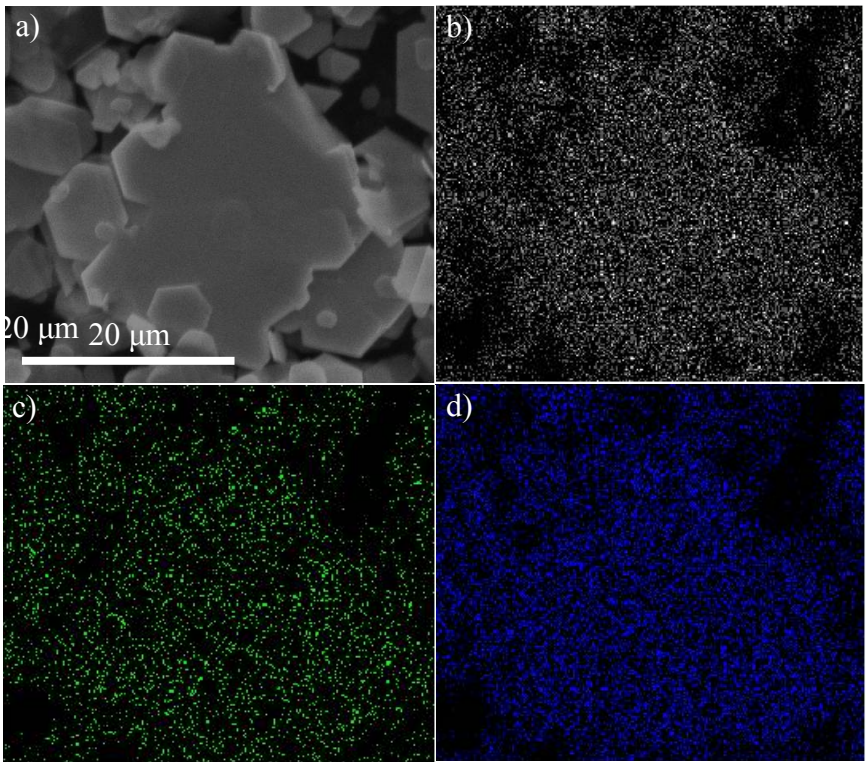


Figure S2.5 SEM micrograph of $WS_{1.4}Se_{0.6}$ (a) and EDX mapping of sulfur (b) , selenium (c) and

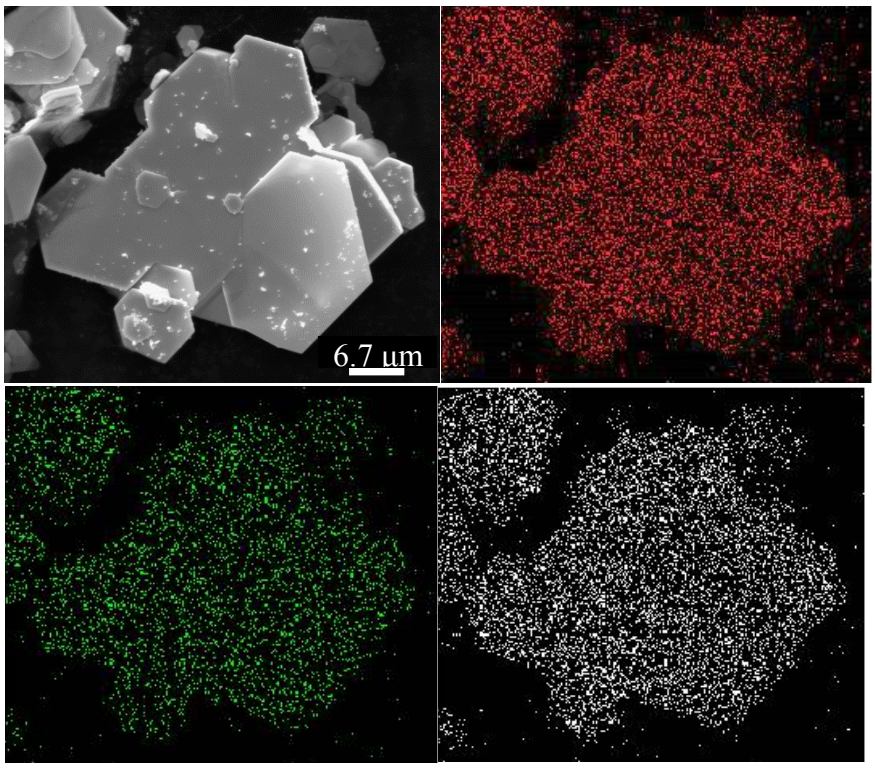


Figure S2.6 SEM micrograph of $WS_{0.8}Se_{1.2}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

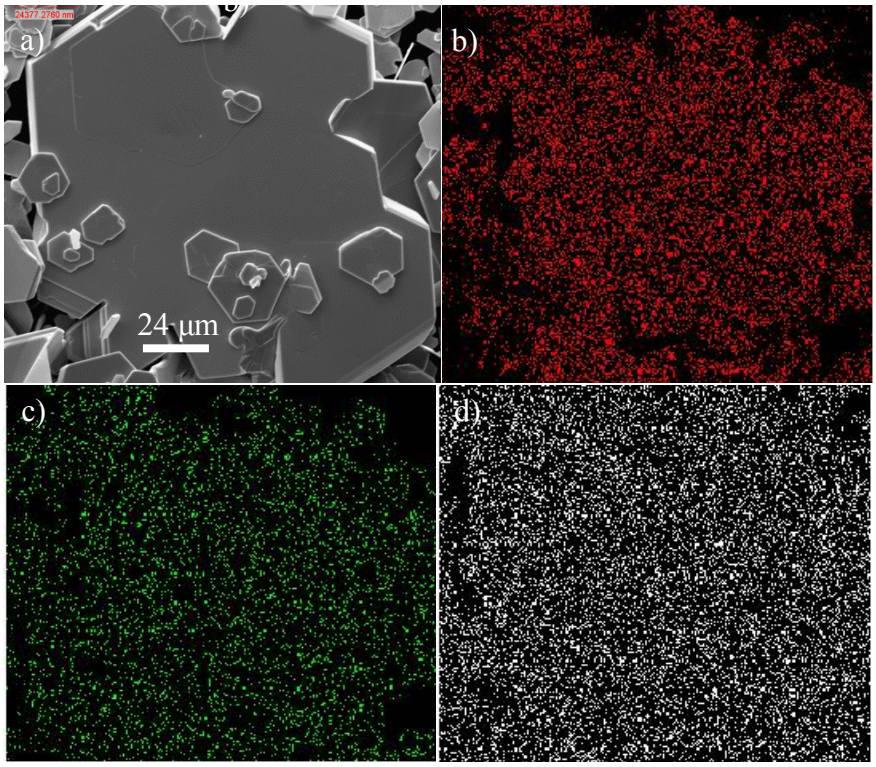


Figure S2.7 SEM micrograph of WSSe (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

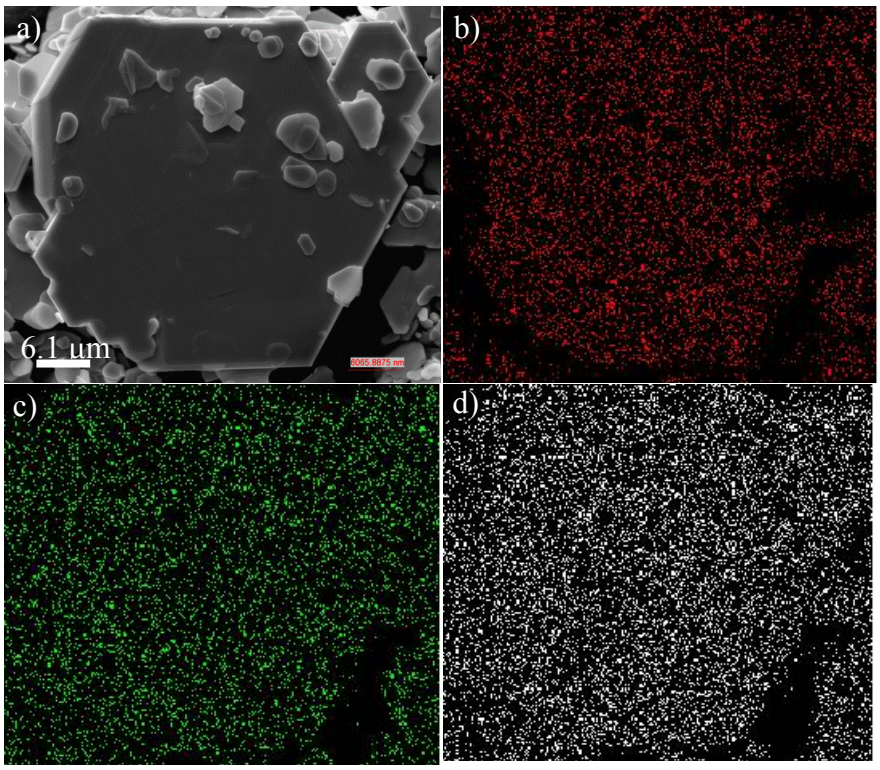


Figure S2.8 SEM micrograph of $WS_{0.4}Se_{1.6}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

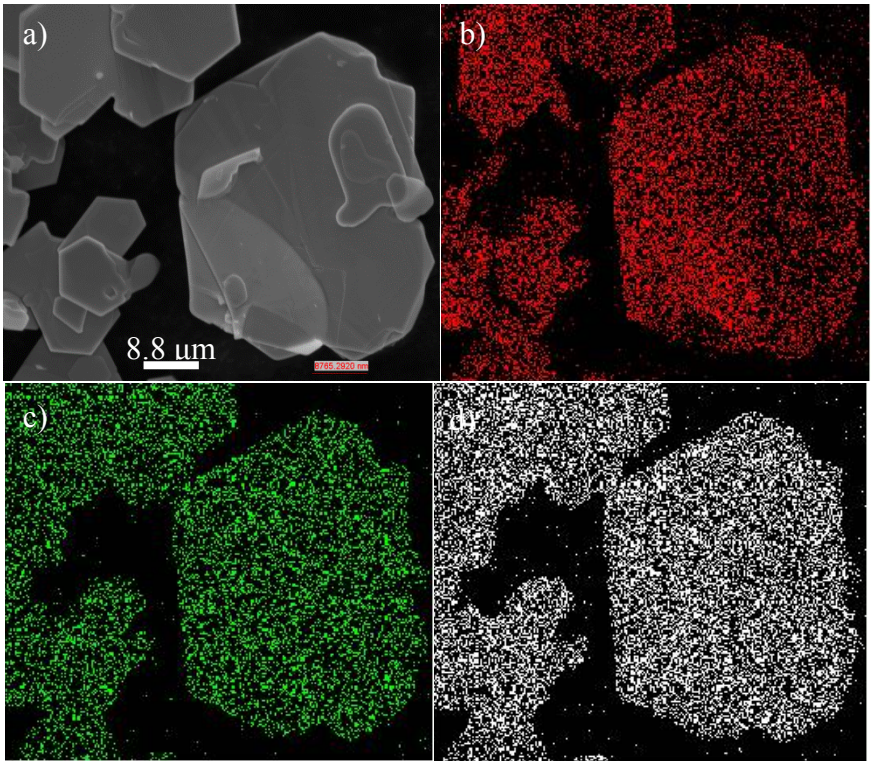


Figure S2.9 SEM micrograph of $WS_{0.6}Se_{1.4}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

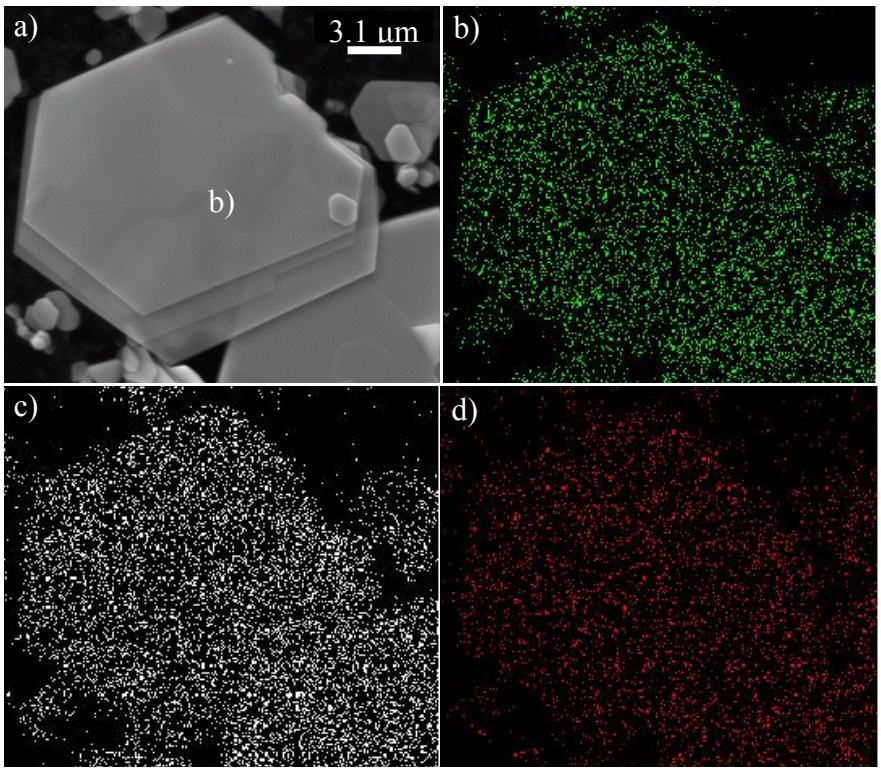


Figure S2.10 SEM micrograph of $WS_{0.2}Se_{1.8}$ (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

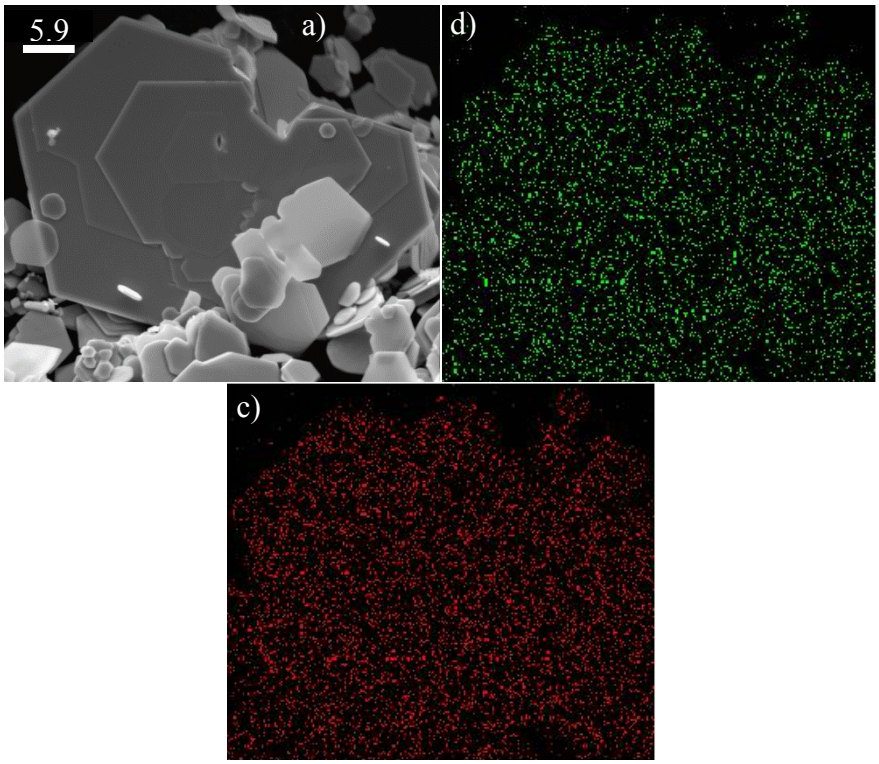


Figure S2.11 SEM micrograph of WSe_2 (a) and EDX mapping of sulfur (b) , selenium (c) and tungsten (d)

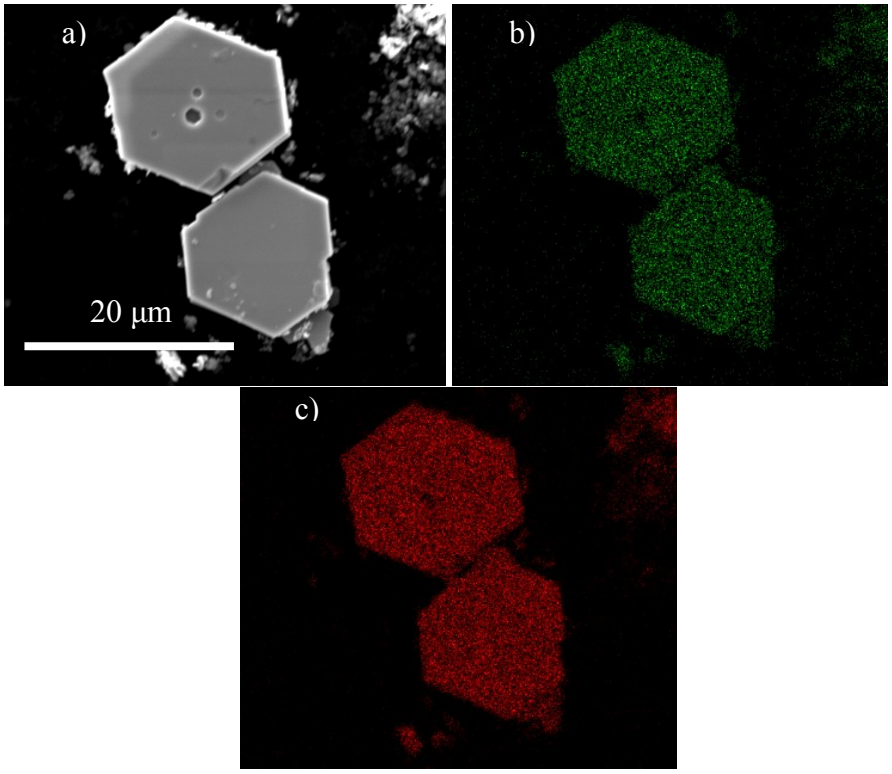


Figure S2.12. SEM micrograph of $MoSe_2$ (a) and EDX mapping of molybdenum (b) and selenium (c)

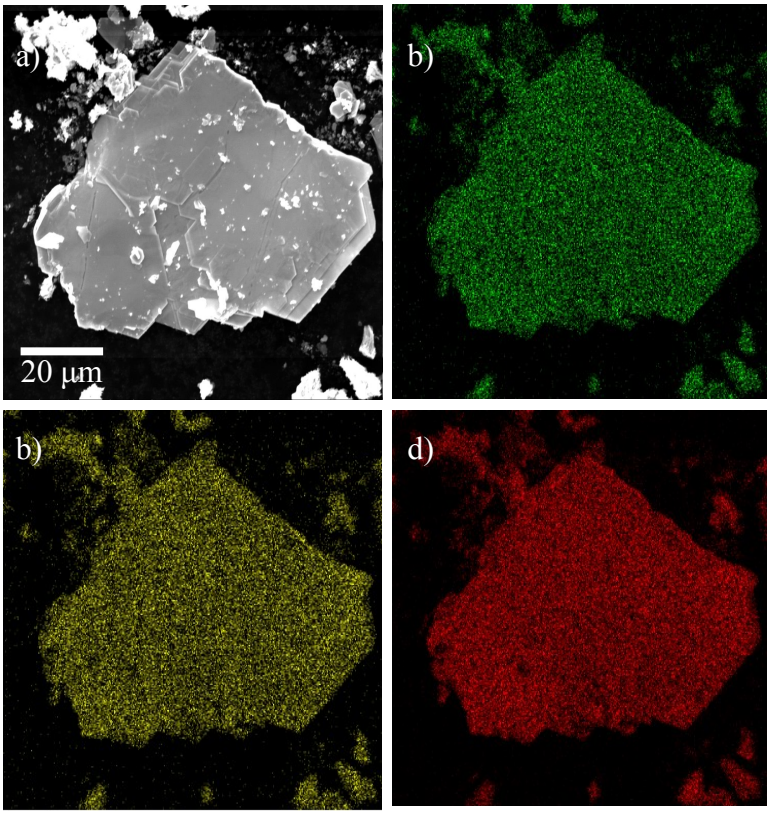


Figure S2.13 SEM micrograph of $MoS_{0.2}Se_{1.8}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

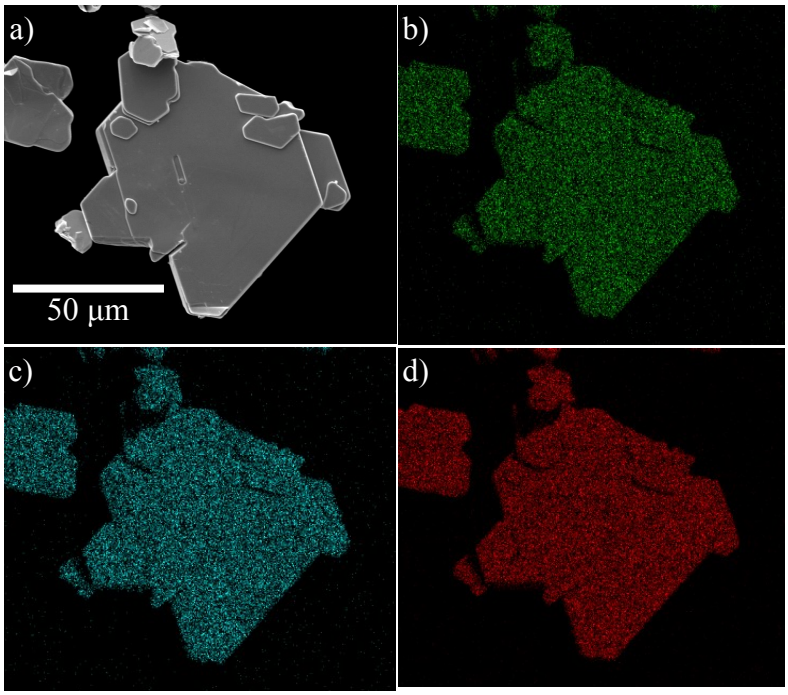


Figure S2.14. SEM micrograph of $MoS_{0.4}Se_{1.6}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

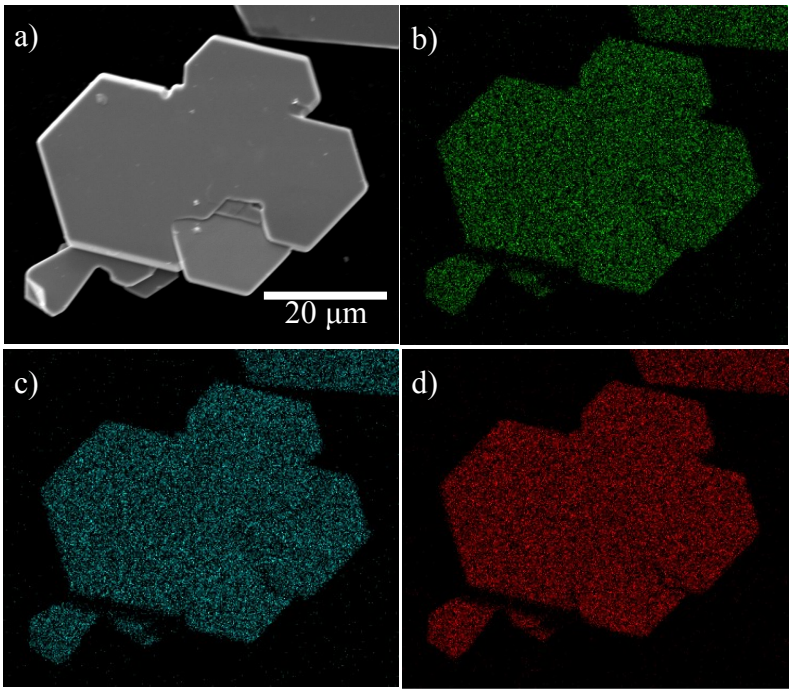


Figure S2.15. SEM micrograph of $MoS_{0.6}Se_{1.4}$ (a) and EDX mapping of molybdenum (b),

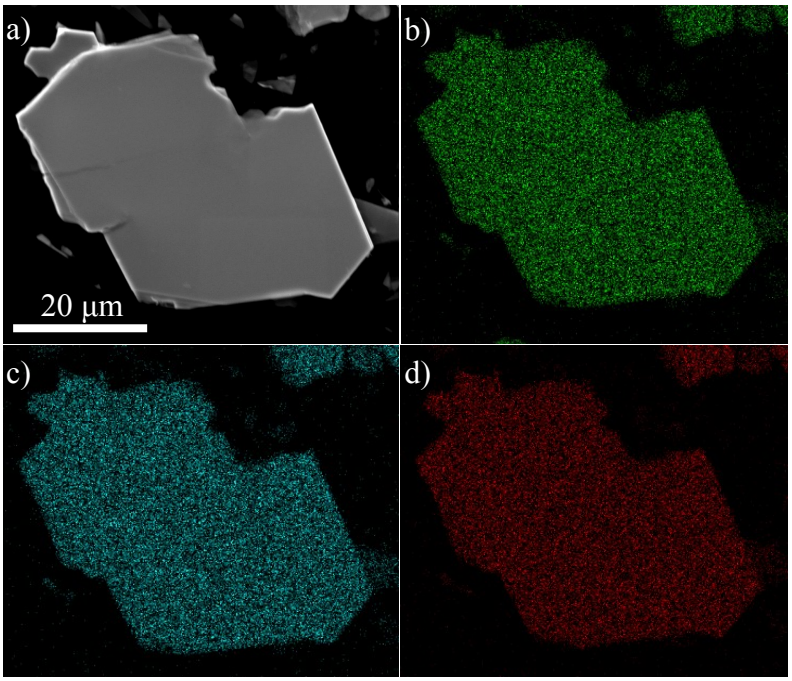


Figure S2.16 SEM micrograph of MoSSe (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

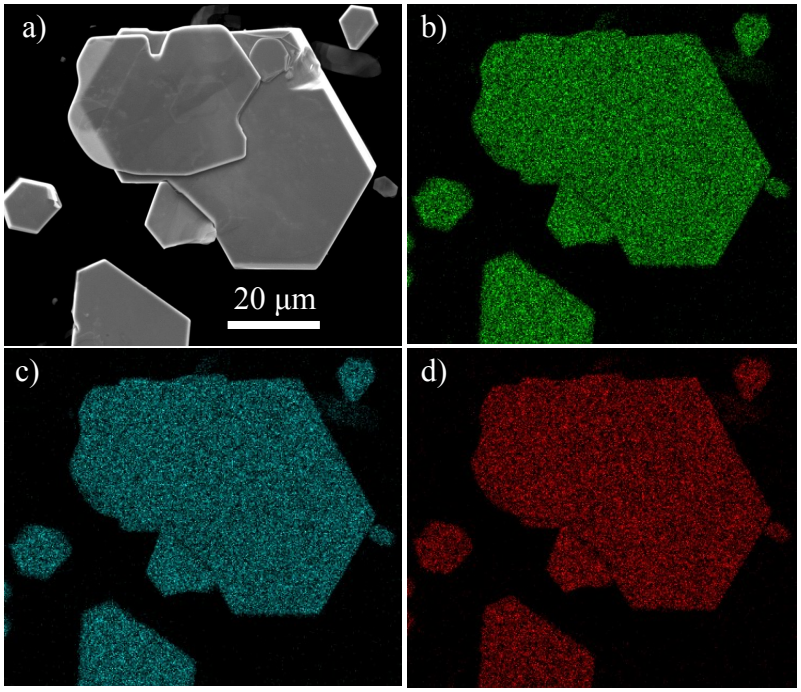


Figure S2.17. SEM micrograph of $MoS_{1.2}Se_{0.8}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

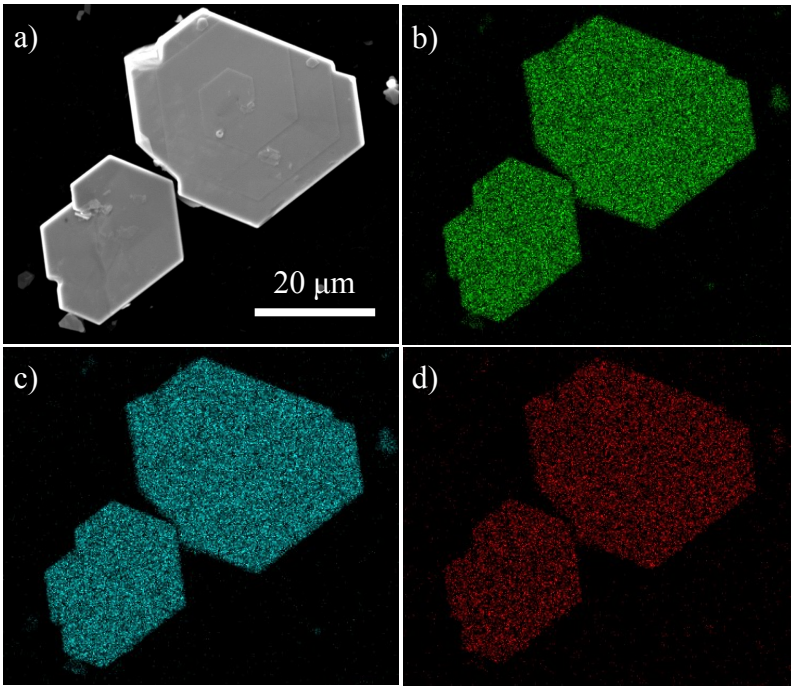


Figure S2.18. SEM micrograph of $MoS_{1.6}Se_{0.4}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

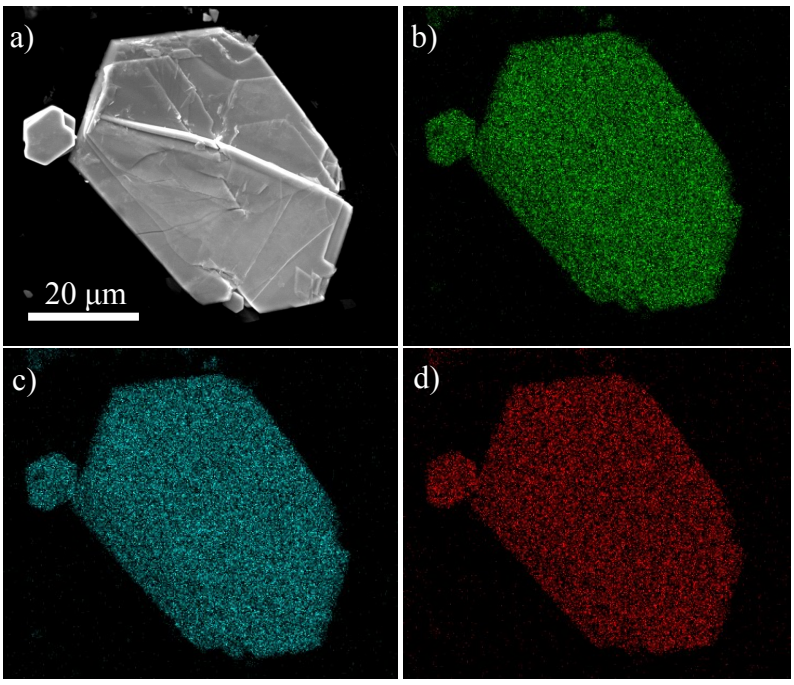


Figure S2.19 SEM micrograph of $MoS_{1.4}Se_{0.6}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

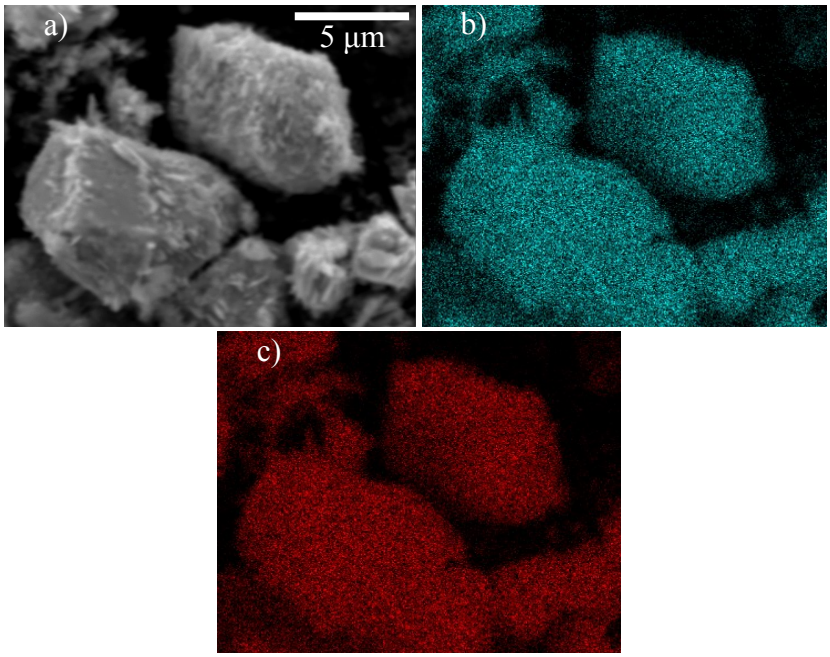


Figure S2.20. SEM micrograph of MoS_2 (a) and EDX mapping of molybdenum (b), sulfur (c)

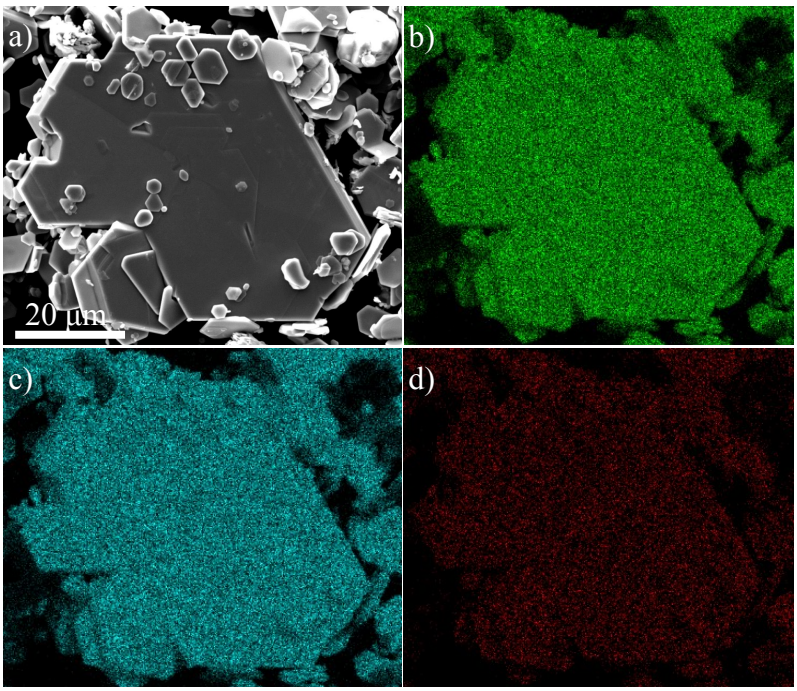


Figure S2.21. SEM micrograph of $MoS_{1.8}Se_{0.2}$ (a) and EDX mapping of molybdenum (b), sulfur (c) and selenium (d)

For each compound, EDX measurements were performed on five different particles. The average atomic percentages and standard deviations are reported in the tables below.

Compound	Concentration (at%)		
	Molybdenum	Sulfur	Selenium
MoS_2	31.0 ± 0.5	69.00 ± 0.5	0
$MoS_{1.8}Se_{0.2}$	31.8 ± 0.8	61.0 ± 1.0	7.2 ± 0.9
$MoS_{1.6}Se_{0.4}$	32.7 ± 2.1	54.6 ± 2.1	12.7 ± 2.3
$MoS_{1.4}Se_{0.6}$	33.5 ± 1.7	45.6 ± 2.5	20.9 ± 2.6
$MoS_{1.2}Se_{0.8}$	31.0 ± 2.8	39.3 ± 3.4	29.7 ± 1.3
$MoS_{1.0}Se_{1.0}$	30.9 ± 3.6	35.1 ± 3.1	34.0 ± 1.8
$MoS_{0.8}Se_{1.2}$	34.4 ± 3.1	26.2 ± 1.8	39.3 ± 3.1
$MoS_{0.6}Se_{1.4}$	32.5 ± 2.1	21.9 ± 2.3	45.6 ± 1.7
$MoS_{0.4}Se_{1.6}$	31.0 ± 3.8	10.5 ± 1.3	58.6 ± 4.3
$MoS_{0.2}Se_{1.8}$	33.2 ± 4.6	7.8 ± 1.5	59.0 ± 3.3
$MoSe_2$	30.5 ± 0.8	0	69.5 ± 0.8

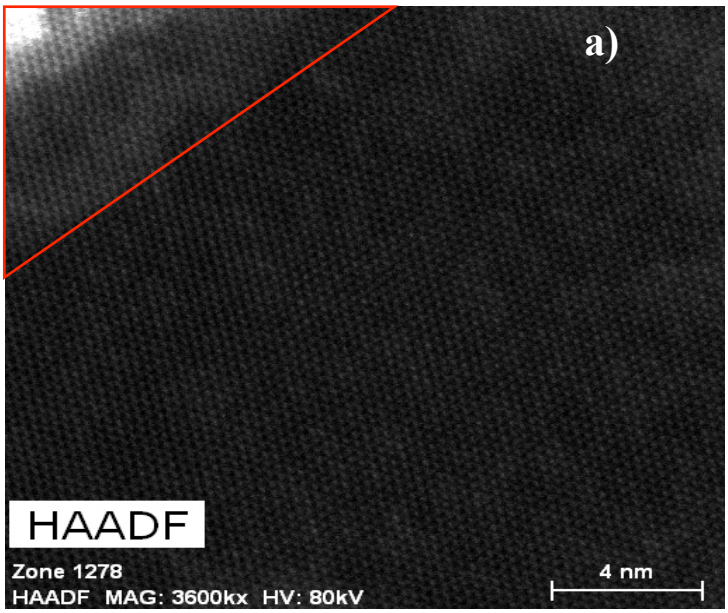
Composition of MoS_xSe_{2-x} solid solutions measured by SEM-EDX.

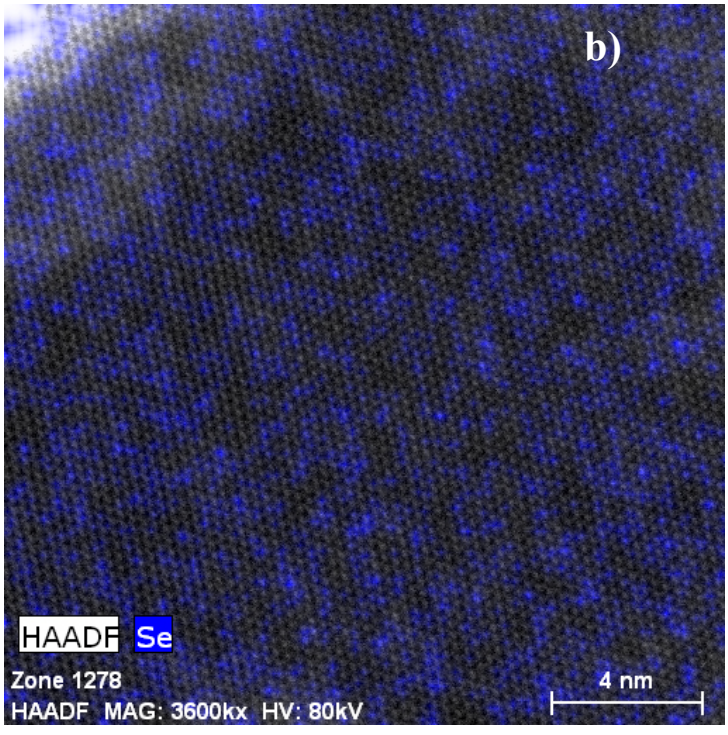
Compound	Concentration (at%)		
	Tungsten	Sulfur	Selenium
WS_2	33.7 ± 0.8	66.3 ± 0.8	0
$WS_{1.8}Se_{0.2}$	32.8 ± 0.6	60.4 ± 1.1	6.8 ± 0.9
$WS_{1.6}Se_{0.4}$	33.5 ± 0.6	53.2 ± 1.0	13.4 ± 0.6
$WS_{1.4}Se_{0.6}$	33.8 ± 0.4	46.5 ± 0.6	19.7 ± 0.5
$WS_{1.2}Se_{0.8}$	33.7 ± 0.7	40.1 ± 1.6	26.2 ± 2.0
$WS_{1.0}Se_{1.0}$	33.0 ± 0.9	32.3 ± 1.9	34.7 ± 2.5
$WS_{0.8}Se_{1.2}$	34.3 ± 0.2	26.7 ± 0.5	39.0 ± 0.6
$WS_{0.6}Se_{1.4}$	33.3 ± 0.7	19.1 ± 0.7	47.6 ± 1.1
$WS_{0.4}Se_{1.6}$	33.2 ± 1.3	12.9 ± 1.0	53.9 ± 1.9
$WS_{0.2}Se_{1.8}$	34.6 ± 0.2	7.3 ± 0.1	58.1 ± 0.2
WSe_2	33.3 ± 1.2	0	66.7 ± 1.2

Composition of WS_xSe_{2-x} solid solutions measured by SEM-EDX.

3. HAADF-EDX mapping of atomic distributions of W, Mo, S, and Se

Monolayer regions were located under the TEM using the high angle annular dark field scanning transmission electron microscope. Elemental EDX mapping of W, Mo, S, and Se was performed on monolayers of $WS_{1.8}Se_{0.2}$. Examples are shown in Figures S3.1 and S3.2.





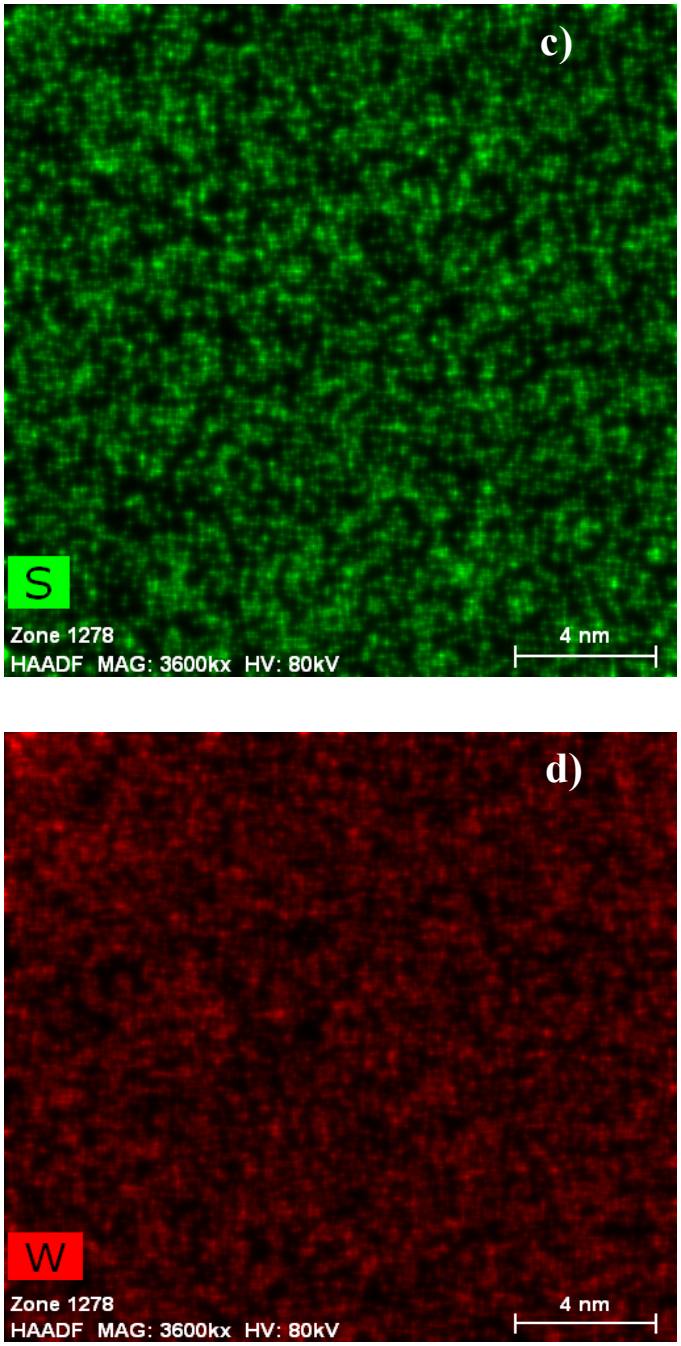


Figure S3.1. a) HAADF-STEM micrograph of $WS_{1.8}Se_{0.2}$. The corner outlined in red is a multilayer region. The rest of the image is a monolayer region. Elemental EDX maps of b) selenium overlayed on the HAADF-STEM micrograph of $WS_{1.8}Se_{0.2}$, c) sulfur d) tungsten.

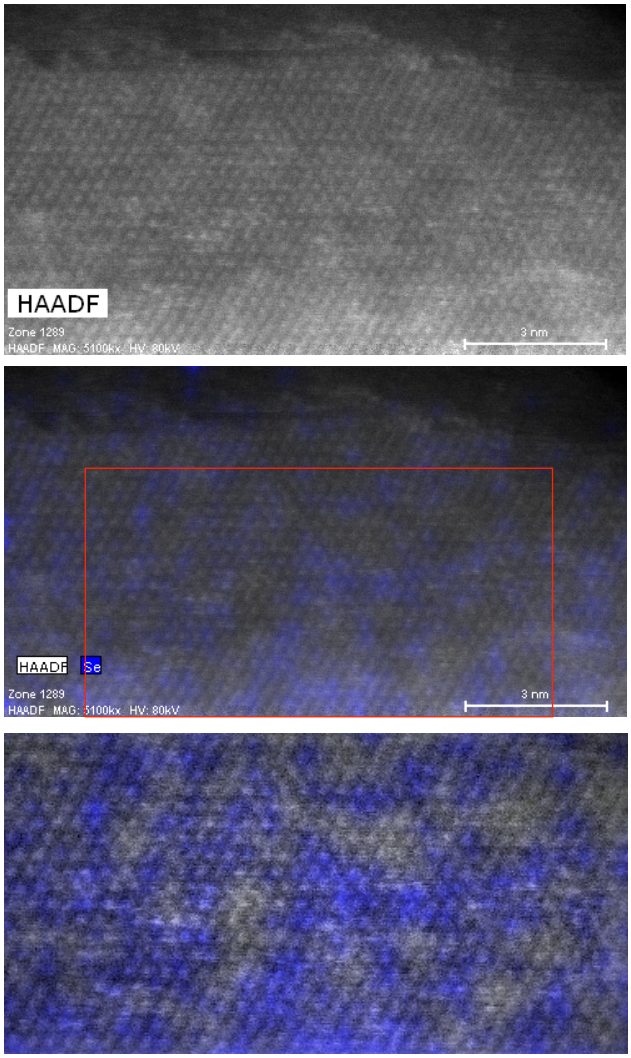


Figure S3.2 a) HAADF-STEM micrograph of $MoS_{1.8}Se_{0.2}$. Elemental EDX maps of b) selenium overlayed on the HAADF-STEM micrograph of $MoS_{1.8}Se_{0.2}$. The red box region in (b) was used for quantifying the degree of clustering within the monolayer. c) The enlarged red box region shown with contrast and brightness adjusted.

4. Calculation of the clustering parameter J from HAADF-EDX data

J was calculated from nearest-neighbor counting data in Fig. 9c according to

$$J = \frac{P_{observed}}{P_{random}} \times 100\%$$

where $P_{observed}$ and P_{random} were obtained from:

$$P_{observed} = \frac{\sum_{i=0}^{6} (i \times N_{gray-i(blue)})}{N_{gray}}$$

and

$$P_{random} = \frac{N_{blue}}{N_{gray} - N_{blue}}$$

Here N_{gray}, N_{blue}, and $N_{gray\text{-}i(blue)}$ are the number of gray-colored metal atoms (coordinated only to sulfur), the number of blue-colored metal atoms (coordinated to one or more Se), and the number of gray-colored W atoms surrounded by i (i = 0 to 6) blue-colored metal atoms, respectively.